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STUDIES ON THE BEHAVIOR OF AMMONIA AND AMMONIUM
SALTS IN THE ATMOSPHERE (1) - FRACTIONAL COLLECTION
OF AMMONIA GAS AND PARTICULATE AMMONIUM

Kiko Kiin, Misturu Fujimura and Yoshikazu Hashimoto

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(1) - FRACTIONAL COLLECTION OF AMMONIA GAS
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| 16. Abstract Atmospheric ammonia gas and ammonium particles were separately collected on a two staged glass fiber filter. The first filter for ammonium collection was a standard glass fiber filter which was washed with distilled water and dried at 120-130°C. The second one for ammonia collection was impregnated with a mixture of 3% boric acid and 25% glycerin solution. The blank of glass fiber filters impregnated with a mixture of the above solution was very low for ammonia, i.e. 0.06 µg in a filter of 47 mm in diameter. The mean concentrations of ammonia and ammonium in air at Kawasaki, a polluted area, were 7.6 and 2.3 µg m ³ , and those at Sanriku, an unpolluted area 0.9 and 0.2 µg m ³ , respectively. The concentrations of ammonia and ammonium at the polluted area were about 10 times higher than those at the unpolluted area. Ratios of concentration levels of ammonium to total ammonia in the atmosphere were 0.3 and 0.2 for the polluted and unpolluted areas, respectively. Ammonium salts in air at both areas were not correlated with relative humidity. | | | |
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STUDIES ON THE BEHAVIOR OF AMMONIA AND AMMONIUM
SALTS IN THE ATMOSPHERE (1) — FRACTIONAL COLLECTION
OF AMMONIA GAS AND PARTICULATE AMMONIUM

Kiko Kiin, Misturu Fujimura and Yoshikazu Hashimoto

Faculty of Engineering, Keio University
3-14-1 Hiyoshi, Kohoku-ku, Yokohama

1. Introduction

It is said that the average concentration of ammonia in the atmosphere environment is 6 ppb [1]. Heretofore, methods of ammonia collection have been the solution absorption method and the sulfuric acid filter method, but problems arise with both of these methods and they are not suitable for measuring variations in time of trace amounts of ammonia. Takafume et al. [2] using glass fiber filters, impregnated with boric acid-glycerin solution (below called boric acid filter), collected ammonia by passing a large volume of air through the filters in a short period of time. Kadowaki et al. [3] using glass fiber filters as prefilters, conducted fractional collection of ammonia and particulate ammonium. However, due to the high blank in the boric acid filters and in the glass fiber filters used for collecting particulate ammonium, the possibility of large errors in the measured values of ammonia and ammonium salts is great, especially in unpolluted areas. The authors, by washing the filters and by heat treatment, have succeeded in reducing the ammonia blank in the boric acid filters and the glass fiber filters used for collecting ammonium salts to one fourth of the previous blank. The treated glass fiber filter and the boric acid filter were mounted on a two stage filter holder and by drawing air in at the rate of 20 liters every two minutes fractional collection of particulate ammonium and gas ammonia was possible. Using this method variations in time of the ppb level of ammonia and ammonium salts were measured in a polluted area and an unpolluted area. The study of the polluted area was conducted November 2-5, 1978, on the roof of the Environmental Health Center in Kawasaki, an extremely polluted area, and the study in the unpolluted area was conducted October 17-19, 1978, at the Rocket Observation station of the Meteorological Agency at

*Numbers in the margin indicate pagination in the foreign text.

Sanriku, Iwate Prefecture, an area very slightly polluted by man.

From these studies we learned that the measurement of ammonia and ammonium gas in the atmosphere is possible using the filter method.

2. The Experiments

2.1 Chemicals and Filters

Glass fiber filters for the collection of ammonium salts: Type A filters of German company make (47 mm in diameter) were steeped in distilled water for one hour after which they were washed with distilled water and dried in an electric dryer (120-130°C).

Boric acid filters for collecting ammonia: Toyo filter papers, type GB-100R (diameter 47 mm) were steeped in distilled water for one hour after which they were washed in distilled water and dried in an electric drier (120-130°C). The filters were then impregnated 1 ml per filter with a 3% boric acid - 25% glycerin solution and dried in a dessicator for 15 minutes.

Sodium phenol nitroprusside solution: Five grams of phenol and 25 mg of sodium nitroprusside were dissolved in 500 ml of water.

Sodium hypochlorite solution: 100/C ml (here C is the percentage of effective chlorine) of sodium hypochlorite and 15 g of sodium hydroxide were dissolved in 1,000 ml of water.

All of the above chemicals were commercial products of special quality.

2.2 Equipment

Holders for the ammonia collectors: Filters were mounted in the two stages on an apparatus of Shintaku manufacture (stainless steel). The first stage was a prefilter for the collection of ammonium salts and the second a filter for the collection of ammonia. A flow meter was connected and an intake pump sucked air in at the rate of 20 liters/min. The effective width of the filters was 43 mm and the length was 120 mm.

Flow meter: The FT/3/8-14-150 model made by Kusano Scientific Instruments was used.

2.3 Operation

The glass fiber filter for the collection of ammonium salts was attached to the first stage of the filter holder and the boric acid filter for the collection of ammonia was attached to the second stage and air was pumped through the filters for two hours at the rate of 20 liters/min.

The ammonia collected by the boric acid filter was extracted with a 0.2% boric acid solution and the ammonium salts collected by the glass fiber filter was extracted with a 0.5% boric acid solution. The ammonium ions in the extracted fluid were measured by the indophenol method [4].

3. Results and Discussion

The boric acid filters used for ammonia collection were impregnated with 3% boric acid. When the ammonia was extracted by 10 ml of 0.2% boric acid solution, the boric acid concentration in the extracted liquid was 0.5%. It is believed that light absorption due to absorption of ammonia was at its maximum value at this time. In order to check the extraction efficiency of the filters, 3 µg/ml ammonia solution was trickled onto the boric acid filters 1 ml per filter and then extracted with a 0.2% boric acid solution. More than 96% of the ammonia was recovered. When distilled water was used as the extraction liquid for the same filter, the extraction efficiency was less than 90%. These results are shown in Tables 1 and 2.

Table 1. Extraction efficiency of ammonia from 3% boric acid-25% glycerin impregnated filters by 0.2% boric acid

| Amount on filter µg sheet | Extraction rates % |
|------------------------------|-----------------------|
| 3.1 | 100.1 |
| 3.0 | 100.0 |
| 3.2 | 100.0 |
| 2.9 | 96.6 |
| 3.0 | 100.0 |
| Mean | 101.1 |
| C.V. % | 1.5 |

Table 2. Extraction efficiency of ammonia from
3% boric acid-25% glycerin impregnated
filters by distilled water

| Amount on filter μg /sheet | Extraction rates % |
|--|-----------------------|
| 2.7 | 90.0 |
| 2.6 | 86.6 |
| 2.6 | 86.6 |
| 2.7 | 90.0 |
| 2.8 | 93.3 |
| Mean | 89.3 |
| C.V. % | 3.1 |

Next a study concerning the blank of the filter used for the fractional collection of ammonia and ammonium salts from the atmosphere was made. For example, the ammonium concentration in the 47 mm diameter glass fiber filter (filter type A) and in the Toyo GB-100R used as the boric acid filter was $0.4 \mu\text{g}$ and $0.35 \mu\text{g}$ per filter respectively. The sulfate concentration was $6.2 \mu\text{g}$ and $10.7 \mu\text{g}$ per filter respectively and the fluctuation in the blank values of the filters was great. As the concentration of ammonia in the air becomes lower the effect on the ammonia blank in the filter becomes greater. Also, it is believed that when the sulfate blank is high, there is a reaction with the ammonia at the time of collection. For this reason, in this experiment, after the filters were well washed in distilled water, they were dried in an electric dryer ($120-130^{\circ}\text{C}$) for about two hours which reduced the ammonium and sulfate blanks in the filters to $0.01 \mu\text{g}$ and $0.1 \mu\text{g}$ per filter respectively. Filters treated in this way were then impregnated with 3% boric acid - 25% glycerin mixture. The ammonium blank in these filters after being dried in a dessicator was $0.06 \mu\text{g}$. Table 3 shows the blank values of ammonium in the boric acid filters.

Table 3. Ammonium concentration in the filters impregnated with boric acid-25% glycerin solution

| Run no. | μg filter (47 mm ϕ) |
|---------|--------------------------------------|
| 1 | 0.07 |
| 2 | 0.05 |
| 3 | 0.05 |
| 4 | 0.04 |
| 5 | 0.06 |
| Mean | 0.06 |

The area in which the studies of the unpolluted area were made was in Sanriku, which is on a peninsula jutting into the Pacific Ocean. The surroundings were forested mountains with no settlements. The area is 20 km southeast of Kanaishi, a steel processing city.

Figure 1 shows the variation in time of concentrations of ammonia and ammonium salts in the industrial area of Kawasaki. The mean concentration of ammonia was 10.7 ppb and that of ammonium salts was 2.3 $\mu\text{g}/\text{m}^3$. Figure 2 shows the variation of the concentration of ammonia and ammonium salts as measured in Sanriku. The mean concentrations of ammonia and ammonium salts were 1.3 ppb and 0.2 $\mu\text{g}/\text{m}^3$ respectively. The concentrations of ammonia and ammonium salts in the industrial area were 10 times higher than that in the unpolluted area.

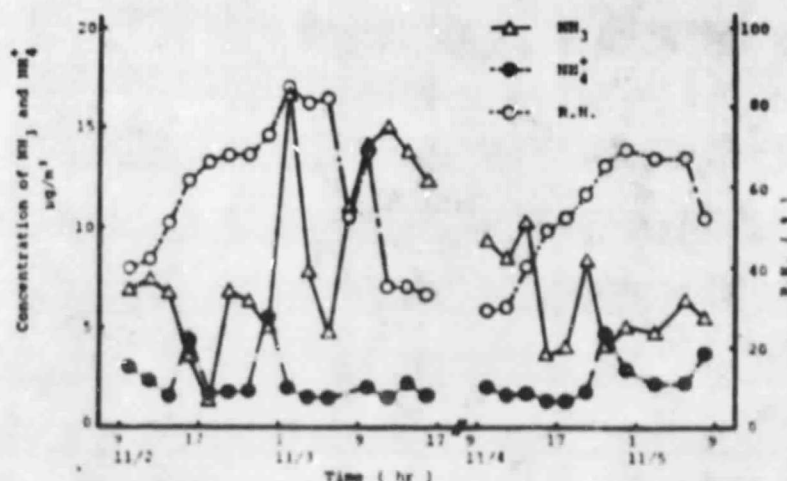
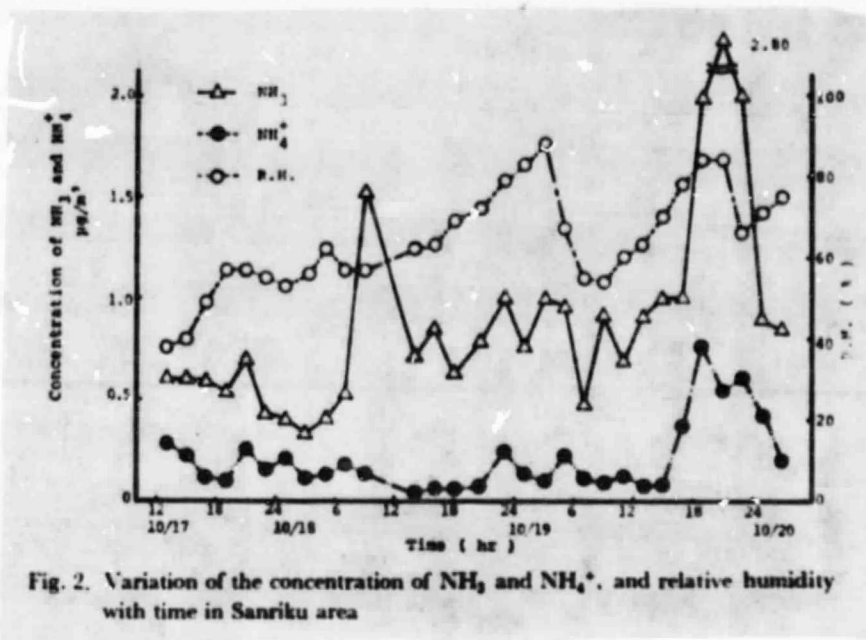


Fig. 1. Variation of the concentration of NH_3 and NH_4^+ , and relative humidity with time in Kawasaki area



It is believed that the ratio of ammonium salts to ammonia in the atmosphere changes according to various conditions, such as the concentration of ammonia and acidic oxides in the area, atmospheric conditions and the seasons. The data on fractional collection of ammonia and ammonium salts in the atmosphere in polluted and unpolluted areas are very few. According to Georgii [5] in polluted areas the ratio is 4-6, the concentration of ammonia being highest. Healy [6] reported that the concentration of ammonium salts was highest at 0.2-0.5. Also it has been estimated that as background concentration in the atmosphere, the ratio of ammonium salts to ammonia is about 4 with the concentration of ammonia highest [1]. By our measurements, in the industrial area the concentration of ammonia was three times that of ammonium salts and in the unpolluted area the concentration of ammonia was five times that of ammonium salts.

The solubility of ammonia in water is extremely high and it is estimated that at more than 95% relative humidity ammonia changes to ammonium very easily in the atmosphere [7]. During the period of our studies the relative humidity at Sanriku was 64% and that at Kawasaki was 57%. The results of calculating the correlation of relative humidity to ammonium in the areas were 0.33 in Sanriku and 0.17 in Kawasaki and there was no correlation between the concentrations of ammonium and relative humidity in either area.

Concerning variation in time of ammonia concentrations in polluted areas, according to Kokubu et al. [8], there is a high concentration during the day. Okita et al. [9] reported that the concentration is highest at night in unpolluted areas. In the areas in which our studies were conducted, no such fluctuation trend was noted. In Sanriku the peak concentrations of ammonia and ammonium salts were at times of no wind (wind velocity 0.0-0.6 m/x). The ammonia peaks in Figure 2 (sic) for Kawasaki are thought to have been generated from sources in the surroundings.

4. Conclusion

The fractional collection of trace amounts of ammonia and ammonium salts in the atmosphere was found to be possible using boric acid filters for ammonia and glass fiber filters for ammonium salts. We were able to lower the ammonium blank in the filters by washing them in distilled water and by heat treatment and were able to keep the fluctuations in the blank constant.

Fractional collection of ammonia and ammonium salts was carried out from the middle of October through the first part of November, 1978 in the unpolluted area of Sanriku in Iwate Prefecture and in the Industrial area of Kawasaki.

The proportion of particulate ammonium accounting for the metallic ammonia was 30% for the industrial area and 20% for the unpolluted area. The concentration of ammonia and ammonium salts was 10 times higher in the industrial area than in the unpolluted area and there was no correlation between the concentrations of ammonia and ammonium salts and the relative humidity in either area.

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